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Catalytic removal of NO_2 by nickel–platinum catalyst supported on multi-wall carbon nanotubes

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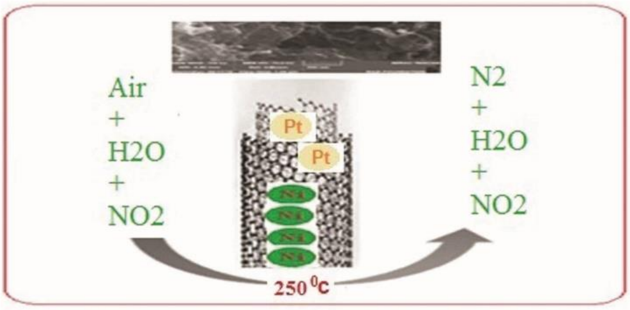
Graphical abstract



Abstract

In the present study, the NO_2 removal efficiency at concentrations of 3000 to 5000 ppm was evaluated by nickel and platinum bimetallic catalyst supported on multiwalled carbon nanotubes (Ni-Pt/MWCNT) along with water vapor at different space velocity and temperatures. Morphological and structural characteristics, material formation phases and catalyst regeneration were investigated by FE-SEM, XRD and TPR tests, respectively. The results showed that increasing the weight percentage of platinum at Ni-Pt/MWCNT catalyst improved the removal efficiency at low temperature. The catalyst 25%W.Ni–3%W.Pt/MWCNT provided 92% removal efficiency at the temperature of 300 °C, space velocity of 25000/hr and concentration of 3000 ppm, while, the 15%W.Ni-5%W.Pt/MWCNT represented highest removal efficiency (70%) at the temperature of 150 °C. The removal efficiency of Ni-Pt/MWCNT catalyst is affected by the weight percentage of nickel and platinum, as well as the NO_2 concentration at various temperatures. The results suggest that H_2O can be used as a reducing agent to reduce NO_2 by produced H^+. The 25%W.Ni-3%W.Pt/MWCNT catalyst removal efficiency at the vicinity of water vapor and concentration of 3000 ppm NO_2, unchanged stability over the period of 100 minute.

Keywords: Catalysis, carbon nanotube, nitrogen oxides, nickel-platinum, air pollution control.

Highlight

- Nickel-platinum based on carbon nanotubes catalyst has the highest hydrogenation rate at 180–200 °C.
- The results of the study indicated the effect of water vapor on the removal efficiency of NO_2 and its reduction by producing H^+.
- Multiwall carbon nanotube catalysts at over concentration 3000 ppm have more than 40% efficiency at temperature 300 °C.
- The removal of NO_2 with Ni-Pt/MWCNT catalysts at weight percent different, space velocity of 25,000/hr is the most cost-effective.
- The highest removal efficiency at 300 °C, concentration of 3000 ppm, space velocity of 15,000/hr for 25%W.Ni-3%W Pt/MWCNT catalyst is 96%.
- During the time period, the catalyst Ni-Pt/MWCNT in during the time period, has a relatively uniform stability the efficiency removal of NO_2.

1. Introduction

Serious concerns have been raised towards the reduction of air quality due to the pollutants emitted from internal combustion engines by increasing transportation and the expansion of industry around the world. Nitrogen oxides resulted from combustion of fossil fuels are one of the most important environmental pollutants that lead to acid rain, Photochemical smog, ozone depletion and the formation of the respiratory system diseases in people (Yu *et al.*, 2016). With increasing the effects caused by the exposure to nitrogen oxides, approaches have been utilized to reduce the release of these pollutants. The use of heterogeneous catalysts is one of the most important and effective ways to reduce the effect of nitrogen dioxide on the environment. In previous studies were used NH_3, HC as

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reducing agents to catalytic reduction NO by release H^+ at low temperatures (Meng *et al.*, 2015). In this study, was used H_2O as a reducing agent to reduce NO_2 to less risky form. The use of the catalytic systems in the automobiles is not effective in reducing the nitrogen oxides by oxygen in the exhaust gas (Wang *et al.*, 2015). Many catalysts, such as various types of transition metal oxide on a variety of bases such as alumina, silica, and titanium have represented an appropriate activity in the SCR process (Xi *et al.*, 2014; Lee *et al.*, 2012). In a study, the catalytic activity of copper oxide with base on zeolite has been reported to be 80% at the temperature range of 300–400 °C (Pereda-Ayo *et al.*, 2014). The use of common catalysts has problems such as low activity, limited strength, high operating temperature range (Li *et al.*, 2012), and reducing the catalytic selective power (Yang *et al.*, 2017; Easterling, 2013). Recently, much attention has been devoted to the development of active catalysts for the development of nanocatalysts activity at low operating temperatures (Guo *et al.*, 2015) to reduce energy consumption and increase the catalytic efficiency by creating a new approach with materials and applying variable methods (Andreoli *et al.*, 2015; Casanova *et al.*, 2015). Carbon materials are often used as catalyst base due to electron transfer properties and good NO_x adsorption (Li *et al.*, 2012; Avalos *et al.*, 2006).

The nanotubes (CNT), due to the high surface area, can provide the possibility for better distribution and aggregation of metal nanoparticles on their surface, as well as increasing the oxygen readsorption from their surface. Readsorption of oxygen from the catalyst surface prevents the saturation of the catalyst surface by oxygen, which increases the selectivity of N_2 compared to N_2O, in catalytic removal of NO_x (Vermisoglou *et al.*, 2011). The use of noble metals, e.g. platinum as an active phase, provides high activation energy and resistance at various temperatures. On the other hand, non-noble metal nanoparticles, e.g., nickel, are more affordable and cheaper than noble metals; and, in other words, they have more activity than some metals, such as copper and iron (Avalos *et al.*, 2006). Previous studies such as “effect of water on catalytic removal of NO” (Xiong *et al.*, 2015) and “selective catalytic reduction of NO with NH_3” (Li *et al.*, 2012) investigated the removal efficiency in the low concentrations (the concentrations lower than 1000 ppm). The use of noble metals in the synthesis of catalysts requires the high costs and the application of non-noble metals is associated with low removal efficiency at high temperatures. On the other hand, studies have shown that the use of bimetallic catalysts has more and longer durability in the NO_x catalyst removal process (Dasireddy *et al.*, 2017). In the previous studies, the presence of water vapor with the ammonia as a reducing agent had a significant catalytic reduction of NO (Xiong *et al.*, 2015), But, in this study, water vapor was used as a reducing agent alone to reduce catalytic NO_2 over time.

In studies, bimetallic catalyst nickel and platinum supported on carbon nanotubes (Ni-Pt/MWCNT) as the catalyst was synthesized in various applications in such cases; the oxygen reduction reaction (Rosado *et al.*, 2016), methanol oxidation (Xiong *et al.*, 2013), carbon monoxide oxidation (Lu *et al.*, 2011). In this study Ni-Pt/MWCNT catalyst was synthesized in various weight percentages with new application as an efficient catalyst, to remove and catalytic reduction of NO_2. Since in various similar studies, different catalysts have been applied to remove NO in low concentrations and there is no study towards the removal of the NO_2 in the high concentration range by the water vapor (as reducing agent), In this study, the Ni-Pt/MWCNT catalyst was used to remove NO_2 as a hazardous and harmful pollutant, and to investigate the effect of variables such as space velocity, concentration, temperature on NO_2 removal efficiencyand determination of optimal condition in weight percent, operational conditions**.**

2. Methods

2.1. Material

All of the chemicals, e.g., potassium tetra chloro platinate (K_2PtCl_4, CAS: 10025-99-7), nickel nitrate hexahydrat Ni(6, CAS: 13478-00-7), ethanol and nitric acid 70% were provided from Sigma-Aldrich. Multiwall carbon nanotubes have been developed as a catalyst base at the Petroleum Research Institute Laboratory under the chemical vapor deposition (CVD) method.

2.2. Acid treatment of multi-walled carbon nanotubes

In order to remove the carbonic impurities, the multi-walled carbon nanotube (MWCNT) was mixed with 70% nitric acid (HNO_3) and was stirred at 120 °C for 4 h. After cooling the acidic solution, it was centrifuged for 15 min at 3000 rpm. The prepared mixture was then filtered and washed with deionized water several times to neutralize the material. Finally, the multi-wall carbon nanotubes were dried in an oven (LAB-OVEN, 10–250) at 70 °C for 12 hr. The second stage of acid treatment was performed to prepare multi-wall carbon nanotubes for final loading of nickel and platinum nanoparticles on nanotubes. At this stage, the dried carbon nanotubes prepared in the first stage were mixed with 2.6 M nitric acid for 5 hours at 110 °C. The resulting mixture was centrifuged for 15 minutes and 3000 rpm, after cooling. After filtration of the mixture, carbon nanotubes were dried in the oven at 60 °C for 12 hours (Dasireddy *et al.*, 2017; Reddy *et al.*, 2010).

2.3. Preparation and synthesis of Ni-Pt/MWCNT nanocatalysts

To prepare the nickel and platinum supported on carbon nanotubes catalyst with different weight percentages, i.e., 15% nickel with 5% platinum on carbon nanotubes and 25% nickel with 3% platinum on carbon nanotubes, the $Ni(NO_3)_3$. $6H_2O$ precursor was mixed in 30 ml of deionized water and then placed in an ultrasonic device for 20 min. the acid treated multiwalled carbon nanotubes were mixed with 50 mL diluted ethanol (alcohol to water ratio of 1:5).

The Ni-containing solution was then added to the multi-wall carbon nanotubes. The obtained mixture was stirred on a thermal heater at 80 °C to obtain a pulpy mixture, and finally the pulpy was placed in an oven at

80 °C for drying the catalyst. Afterward, the K_2PtCl_4 precursor was mixed in 30 ml of ethylene glycol and was placed in the ultrasonic apparatus for 15 min for more dissolution of materials. The solution containing platinum nanoparticles was added to the container of multi-wall carbon nanotubes powder. The obtained mixture was heated on a thermal heater at 90 °C for 6 h. Then, a certain amount of ethanol and deionized water were used to material for stabilization of the platinum nanoparticles on carbon nanotubes. Finally, the mixture was dried in an oven at 70 °C. The calcinations of the Ni-Pt/MWCNT catalyst powder was carried out in the thermal furnace (SHIMIFAN F.47) at 400 °C for 3 hours.

2.4. Characterization of nano-catalyst

The structural characteristics of the catalyst samples were determined using the scanning electron microscope (SEM, TESCAN MIRA3 model) with a magnification of 200 nm. The X-ray diffraction instrument (XRD, EXPLORER model) and a 0.03-ampere copper lamp with the wavelength of 0.154 nm were used for identification of the produced phases of nickel-platinum catalyst supported on multi-wall carbon nanotubes. The diffraction pattern of samples was recorded in the 2ϑ range between 5 and 80 degrees. The temperature-programmed reduction (H_2-TPR) was accomplished on the fixed bed reactor of 20 mg of the powdered catalyst by the flow of gas mixture consisted of 5% hydrogen with argon gas and air flow rate of 0.02 liters per minute at heating temperature of 10 °C. The reduction levels of the outlet hydrogen were measured by Micromeritic 2900 with the thermal conductivity detector (TCD). The semi-quantitative investigation and identification of nickel and platinum particles and the weighing of particles were carried out using Energy-dispersive X-ray spectroscopy (EDS, SAMX model) with a magnification of 200 µm and an energy spectrum of 15 KeV. Investigation of functional groups produced on the structure of multi-wall carbon nanotubes after acid oxidation and synthesis of Ni-Platinum nanoparticles on the carbon nanotube was performed by Fourier Transform Infrared Spectrometer (FTIR) Model PERKIM ELMER Spectrom 2.

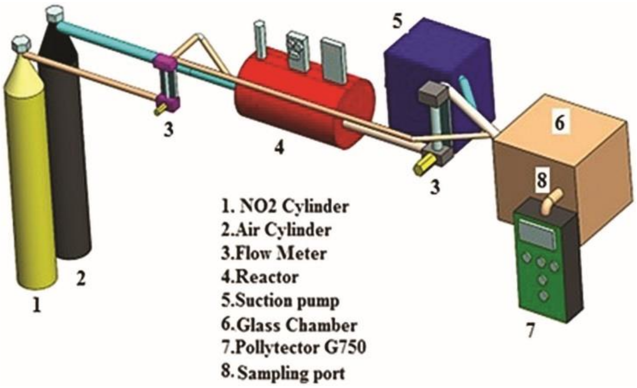


Figure 1. Schematic of experimental set-up for catalytic elimination

2.5. The method of catalytic reactor tests

In order to verify the NO_2 removal efficiency by synthesized catalysts in different operating conditions, the reactor system shown in Figure 1 was designed and launched.

A quartz reactor (length of 25 cm and diameter of 0.8 cm) equipped with an operational temperature control sensor, was used to locate the catalyst and to carry out the NO_2 removal process. The gas flow was initially passed through the volumetric flow controller (LZB Rotameter 6–60 ml) to estimate the volume of the inlet gas. The air flow with 28% moisture was passed through the catalyst bed in the reactor. The humidity check sensor (TFA dost MANN/WER THEIM) was used to measure the inlet and outlet moisture content. To regulate the temperature of the reactor in the range of 100–300 °C, a heating furnace equipped with a controller system was used. In each test, 300 mg of the powdered catalyst with neutral ceramic rocks were embedded in the reactor. The flow rate passing through the catalyst bed was determined to 2 Lit/min, 2.6Lit/min and 3.2 Lit/min, according to the space velocities of 15000, 20000 and 25000/hr, respectively; it is calculated based on the following equation:

$$\text{Space Velocity} = Q / V$$

In the above relation, V is the volume of the catalyst (m^3), and Q is the volume flow rate (m^3/h). The inlet concentrations to the reactor were 3000.4000 and 5000 ppm. A gas meter device (Pollytector G750) equipped with an electrochemical NO_2 sensor with an error of ±0.5 has used for measure of outlet concentration of NO_2 from the reactor. The blower pump (DUST SAMPLER L60 240 V) was used to dilute the outlet gas flow, and the glass chamber was applied to uniform the outlet gas concentration and to measure the outlet NO_2. Equation 2 is utilized to determine the NO_2 removal efficiency by synthesized catalysts.

$$\text{Efficiency (\%)} = (([NO_2]_{in} - [NO_2]_{out}) / [NO_2]_{in}) \times 100 \qquad (1)$$

3. Results and discussion

3.1. X-ray diffraction pattern (XRD)

The X-ray diffraction pattern of the synthesized catalysts is shown in Figure 2. The peak of the multi-dimensional structure of the multi-walled carbon nanotubes (002) at 26° shows the amorphous structure and high electrical conductivity. Scattered peaks at 46.2, 67.6, 37.24, and 62.62 correspond to platinum crystalline nanoparticles which the face-centered-cubic are 111, 200, 220, 211, and 224, respectively (Joung *et al.*, 2014). The scattered peaks of Ni nanoparticles at 43.07, 75.23 and 39.69 are 111, 022 and 121 in the face-centered-cubic, respectively (Adekunle *et al.*, 2014). Comparison of the two graphs A and B shows that, with increasing nickel content and decreasing the amount of platinum, the peak related to $2\vartheta = 43.07$ was increased and the peak at $2\vartheta = 62.6$ was reduced, which is consistent with the increasing and decreasing the amount of nickel and platinum in the synthesis of the catalyst. On the other hand, the peak at 26° related to the diffraction angle of carbon nanotube has decreased, which is indicative of a decrease in the crystalline surface of the base material. However, in both cases, the presence of nickel and platinum particles separately on the surface of the material is shown, which is consistent with the results of the studies conducted by Hashemi *et al.* (2017) and Rosado *et al.* (2016). The average particle size of 15%W.Ni-5%W.Pt/MWCNT catalyst and 25%W.Ni-3%W.Pt/MWCNT in Table 1 is approximated by equation 1 of the SCHERRER equation.

$$d = (0.9 \times \lambda) / (B_{2\theta} \times Cos\theta_{Max}) \qquad (2)$$

The largest size (53 nm) was observed for the 25%.W.Ni-3%.W.Pt/MWCNT catalyst and the smallest size was observed to be 14 nm and was related to the 15%.W.Ni-5%.W.Pt/MWCNT catalyst.

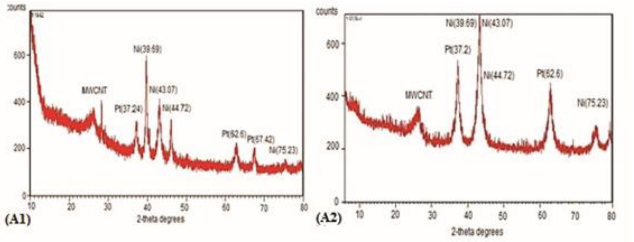


Figure 2. X-ray diffraction (XRD) pattern (A1) Ni-Pt/ MWCNT That 3%W.Pt and 25%W.Ni (A2) Ni-Pt/ MWCNT That 5%W.Pt and 15%W.Ni

Table 1. Pt, Ni particle sizes calculated from XRD peaks

Peak position (2*θ*)	**Miller indices**	**Weight percent of Ni,Pt(15,5)**		**Weight percent of Ni,Pt(25,3)**	
		FWHM	**Grain size(nm)**	**FWHM**	**Grain size(nm)**
37.24	211	0.2362	35	0.1574	53
43.07	111	0.059	30	0.1968	43
62.6	224	0.63	14	0.8659	10
67.42	220	0.39	23.89	0.7872	11
75.23	022	0.63	15	0.9446	10

3.2. The results of scanning electron microscopy (FE-SEM)

3.2.1. X-ray spectroscopy (EDS)

The EDS analysis of the base catalyst (MWCNT) and synthesized catalyst in Figure 3 shows the presence of nickel, platinum, carbon nanoparticles, and minor amounts of oxygen and chlorine. The load level and the calculated weight percentage of the catalysts were shown in Table 2. The weighing of matter in each sample indicates the presence of nickel and platinum, with different weight percentages, in the catalyst structure; based on the results, the 15%.W.Ni-5%.W.Pt/MWCNT catalyst has 14.25% nickel and 4.13% platinum and the 25%.W.Ni-3%.W.Pt/MWCNT catalyst contains 7.09 W% platinum and 23.68 W% nickel. This reduction in the amount of nickel and platinum can be due to a semi-quantitative X-ray machine or a lack of distribution of nickel and platinum on the catalyst base. These results were consistent with Hosseini *et al.* (2017).

Table 2. Weight percent Ni and Pt in way tree catalyst

Catalyst type	**Element**					
	% W C	**%W O**	**% W Cl**	**% W Ni**	**% W Pt**	**% W total**
MWCNT	85.11	14.89	-	-	-	100.00
(% W.5–15) Pt-Ni/MWCNT	65.29	12.23	4.10	14.25	4.13	100.00
(%W. 3–25) Pt-Ni/MWCNT	63.08	4.00	2.15	23.68	7.09	100.00

3.2.2. Results of temperature-programmed reduction (H_2-TPR)

The results of TPR test for MWCNT and Ni-Pt/MWCNT catalysts with different weight percentages of nickel and platinum were shown in Figure 4. The comparison of the active centers on the synthesized catalysts illustrated that the catalyst with 25 %w/w weight percentage of nickel and 3%w/w of platinum was more active in the temperature reduction, compared to the catalyst with 15%w/w of nickel and 5%w/w of platinum, since the 25%W.Ni-3%W.Pt/MWCNT catalyst has the highest hydrogen consumption at 200–300 °C; and on the other hand, it is indicative of further interaction between nickel and platinum particles with the surface of carbon nanotubes. As shown in Figure 4, the highest hydrogenation of carbon nanotubes is in the range of 500–700 °C. By adding the nickel and platinum nanoparticles, the hydrogenation temperature was dropped to 200 °C. The hydrogenation temperature of Ni nanoparticles in the reduction process was observed at 350–400 °C and the reduction temperature of platinum nanoparticles was at 200 °C, which is consistent with the results of Suhong Lu *et al.* (2011) and KO *et al.* (2006). The TPR graphs related to nickel and platinum catalysts based on carbon nanotubes have three temperature reduction peaks. In Ni-Pt/MWCNT catalysts, the reduction peak around 200 °C is due to the reduction of platinum and nickel ions. Studies have shown that platinum metal in the vicinity of metal oxides can lead to catalytic reduction at low temperatures (Li *et al.*, 2007).

Platinum is reduced at lower temperatures; this reduction can reduce nickel oxides at low temperatures by reducing ion Platinum. Temperature reduction peaks at 350 °C can indicate a reduction in nickel oxides and a peak reduction related to the temperature of 500 °C is attributed to a reduction in nickel ions that have a stronger interaction with the base surface (Lu *et al.*, 2011; Maitarad *et al.*, 2014).

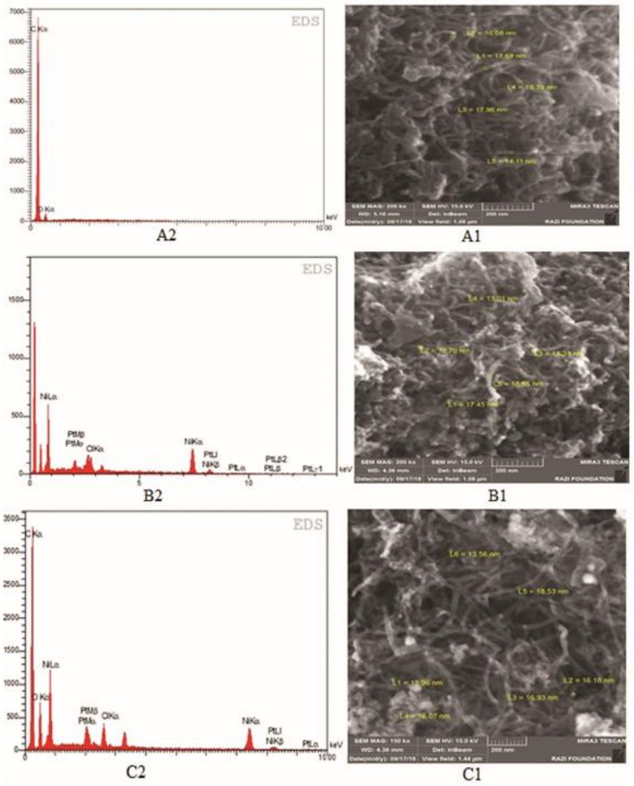


Figure 3. Field emission scanning electron microscopy (FE-SEM) image. (A1)MWCNT, (C1) Ni-Pt/ MWCNT That 5%W.Pt and 15%W.Ni, (B1) Ni-Pt/MWCNT That 3%W.Pt and 25%W.Ni.energy dispersive X-ray spectroscopy (EDS) spectra of catalyst(A2) MWCNT (C2)Ni-Pt/ MWCNT That 5%W.Pt and 15%.W.Ni, (B2) Ni-Pt/ MWCNT That 3%W.Pt and 25%.Ni

3.2.3. Fourier-transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy related to multi-walled carbon nanotubes treated with acid and synthesized catalysts were represented in Figure 5. The peak appearing at 3400–2800 cm^{-1} (2926 cm^{-1}) is related to the formation of the oxygen-containing functional groups of the carboxyl group (R-COOH), which appears in all three graphs. The peak at 1170 cm^{-1} represented in Figure 6A1 is related to the carbon structure with the hybridization of SP3 (Poorkhalil *et al.*, 2015). The peak at 1610–1550 cm^{-1} is related to the carboxyl group (R-CO-O-). The results observed in the study by Pour khalil *et al.* revealed that the existence of oxygen-containing functional groups on carbon nanotubes in the MnO_x/MWNT catalyst increased the selectivity of N_2 and, on the other hand, the conversion efficiency of NO_X (Li *et al.*, 2007). The result of the FTIR experiments revealed the presence of oxygen-containing functional groups in the synthesized catalyst (Ni-Pt/MWCNT) and base catalyst (MWCNT).

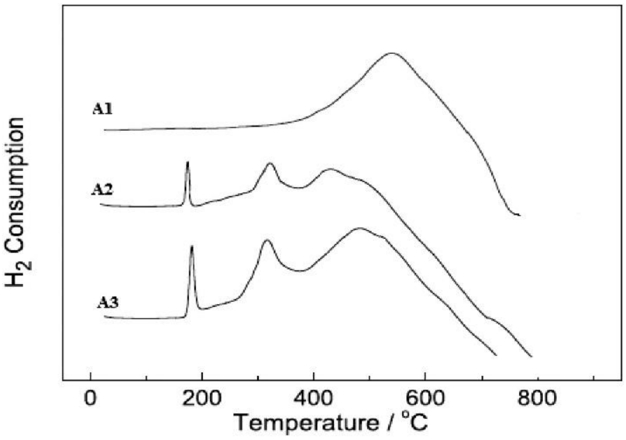


Figure 4. TPR Profile Of (A1)MWCNT (A2)15%W.Ni-5%W.Pt based on MWCNT (A3)25%W.Ni- 3%W.Pt based on MWCNT

3.3. Catalytic removal

Evaluation of water vapor levels at the outlet of reactor containing the catalyst bed of 25%W.Ni-3%.W.Pt/MWCNT showed that the moisture content reduction was 18% at 150 °C and it reduced to 19% at 300 °C. As shown in the chemical reactions in the catalytic reduction section, a chemical reaction product in the chemical reactions can be water molecules; the production of these water molecules can be effective in increasing the catalytic reduction efficiency by increasing the temperature. It should be noted that the XRD images of the Ni-Pt/MWCNT catalysts revealed the presence of the impurities and a part of the catalytic activities of the catalysts may be due to the presence of these impurities. Since the effect of these impurities compared to nickel and platinum particles with higher weight percentages in catalytic activity can be neglected.

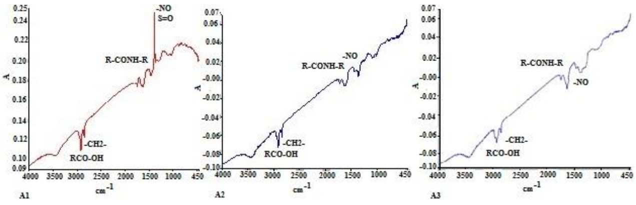
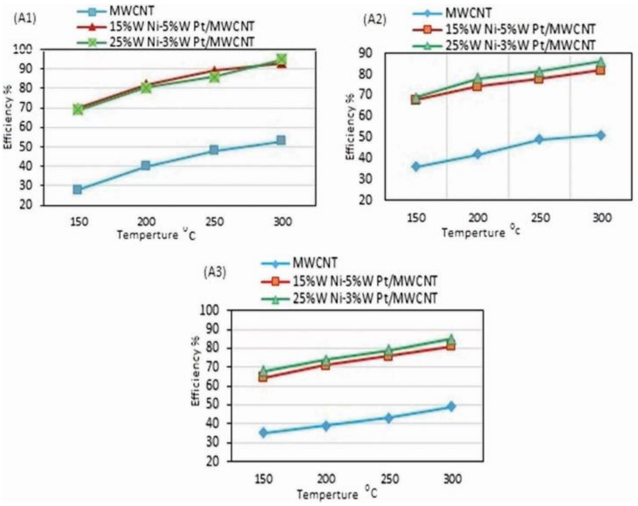


Figure 5. FTIR Profile Of (A1) MWCNT (A2)15%W.Ni-5%W.Pt based on MWCNT (A3)25%W.Ni- 3%W.Pt based on MWCNT

3.4. Effect of temperature on NO_2 removal efficiency by Ni-Pt/MWCNT catalyst

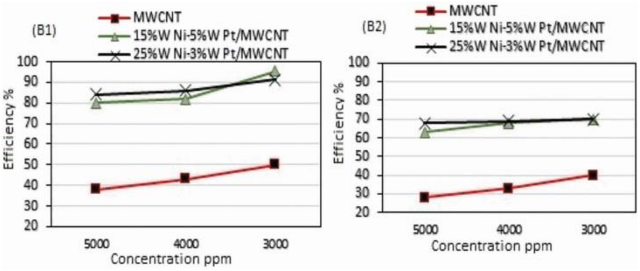
Temperature is one of the effective factors in increasing the efficiency of chemical reactions and, on the other hand, increasing the chemical equilibrium constant and the number of collision between the reactant molecules on the catalyst bed. According to Arrhenius, increasing the temperature and reducing the activation energy are led to developing the speed of a chemical reaction to produce the final product.



Figur 6. NO_2 removal efficiency profiles over prepared catalysts MWCNT, 15%W.Ni-5%W.Pt/MWCNT, 25%W.Ni-3%W.Pt/MWCNT at a space velocity of 25000/hr and temperature 150, 200, 250, 300 °C and (A1) concentration of 3000 ppm (A2) concentration of 4000 ppm (A3)concentration of 5000 ppm

The results of NO_2 catalytic removal tests at different temperatures, the space velocity of 25000/hr and concentrations of 3000, 4000 and 5000 ppm were represented in Figure 6 and revealed that increasing the temperature enhances the NO_2 removal efficiency. At concentrations of 3000 and 4000 ppm, increasing the efficiency (i.e., the slope of A1 and A2 in Figure 6) was greater at lower temperatures compared to the high temperatures. Pour khalil studied the catalytic reduction of NO with NH_3 by the MnO_x/CNT catalyst at 300 °C and NO concentration of 900 ppm and space velocity of 30000/hr, and reported the removal efficiency of 95%, which it is indicative of the high efficiency of the catalyst (Poorkhalil *et al.*, 2015). This increase is due to the studied concentration and amount of the catalyst. In present study, the NO_2 removal efficiency was obtained to be 91% at the temperature of 300 °C and lowest concentration of NO (3.3 times the concentration of NO in Khalil pour). Similarly, Li *et al.* conducted a study to assess the efficiency of catalytic removal of NO using the reducing agent of NH_3 and their results revealed that increasing the temperature is led to enhance the NO removal efficiency (Li *et al.*, 2012), which is similar to the results of the present study. The CuO_x/CNT catalyst offers the NO removal efficiency of 67% at temperature of 250 °C, concentration of 700 ppm and a speed velocity of 7500/hr, which it has less removal efficiency compared to the results of this study; in this study, the removal efficiency was obtained to 90% at concentrations above 3000 ppm and space velocity of 25000/hr, which indicates the high efficiency of Ni-Pt/MWCNT catalyst compared to the Cu/CNT catalyst.

The highest removal efficiency (78%) was obtained by 25%W.Ni-3%W.Pt/MWCNT catalyst at 150 °C and the lowest efficiency (28%) was obtained using the MWCNT catalyst. The highest efficiency using the 25%W.Ni-3%.WPt/MWCNT and 15%W.Ni-5%W.Pt/MWCNT catalysts was achieved to be 91% at 300 °C. The removal efficiency of the MWCNT catalyst can indicate the presence of impurities and, on the other hand, the presence of oxygen containing functional groups on the substrate.



Figur 7. NO_2 removal efficiency profiles over prepared catalysts MWCNT, 15%W.Ni-5%W.Pt/MWCNT, 25%W.Ni-3%W.Pt/MWCNT at a space velocity of 25000/hr and concentration of 3000, 4000, 5000 ppm and (B1) temperature of 300 ° C (B2) temperature of 150 °C

3.5. Effect of concentration on catalytic removal efficiency of NO_2

The results of NO_2 removal experiments at various concentrations, temperatures of 150 and 300 °C and space velocity of 25000/hr were brought in Figure 7 and clarified that, increasing the concentration decreased the removal rate obtained by the Ni-Pt/MWCNT catalyst with different weight percentages of nickel and platinum. One of the reasons for increasing the chemical reaction rate is the increase in the concentration of the reactants in a chemical reaction. However, since the required amount of activation energy is not provided for the reactants to form the active compound and to carry out the chemical reaction, increasing concentration reduces the conversion efficiency of the reactants to the products. The results of the removal efficiency at various concentrations indicate that, by increasing the concentrations, the removal efficiency is not reduced to the same extent (there is no linear relationship between the increase in efficiency and the decrease in concentration) but reducing the removal efficiency was less in comparison with increasing the concentration. In general, Ni-Pt/MWCNT catalysts had a 45% increase in efficiency compared to the MWCNT catalyst.

The 25%W.Ni-3%W.Pt/MWCNT catalyst had higher removal efficiency at a concentration of 4000 and 5000 ppm compared to the 15%W.Ni-5%W.Pt/MWCNT catalyst. By reducing the concentration, the removal efficiency of the 15%W.Ni-5%W.Pt/MWCNT catalyst is greater than the 25%W.Ni-3%W.Pt/MWCNT catalyst; so that, at high temperatures, it can represent the removal efficiency of 95% and, at a low temperature, its removal efficiency is 70%. By comparing the results obtained at different concentrations, it can be concluded that the 25%W.Ni-3%.W.Pt/MWCNT catalyst has higher removal efficiency than 25%W.Ni-3%W.Pt/MWCNT catalyst at high temperatures and concentrations and, at lower temperatures, the catalyst with a higher weight percentage of platinum has higher removal efficiency at lower concentrations. These results are affected by the percentage of active centers of catalyst in different conditions. The removal efficiency is higher at low concentrations than the high concentrations, which the results of similar studies are indicative of reducing the changes of removal efficiency at lower temperatures, compared to high temperatures, with increasing concentrations (Xiong *et al.*, 2015).

3.6. Effect of space velocity on efficiency of Ni-Pt/MWCNT catalyst

The results of catalytic removal experiments at the temperatures of 150 and 300 °C, concentration of 3000 ppm and different space velocities were represented in Figure 8 and revealed that increasing space velocity reduced the removal efficiency. The highest removal efficiency (98%) using 25%W.Ni-3%W.Pt/MWCNT was obtained at a space velocity of 15000/hr and at a high temperature. The lowest efficiency (28%) was achieved by MWCNT at the space velocity of 25000/hr and at the low temperatures; in this space velocity, the highest efficiency for 25%W.Ni-3%W.Pt/MWCNT catalyst was obtained to be 92% at the high temperatures. The 15%W.Ni-5%W.Pt/MWCNT catalyst was able to provide the removal efficiency of 97% at the space velocity of 15000/hr and high temperatures, while its removal efficiency was 91% at the space velocity of 25000/hr. The results were indicative of 1% difference between Ni-Pt catalysts with different weight percentages at a space velocity of 25000/hr. The results of similar studies showed that by increasing the space velocity from 30000/hr to 120000/hr, the removal efficiency was reduced by 80–70% (Xiong *et al.*, 2015). Compared to this, increasing the space velocity in the present study has not led to significant changes in removal efficiency because the range of space velocity is not high; but, on the other hand, this study indicates the significant effect of velocity speed on the overall the removal of NO_2.

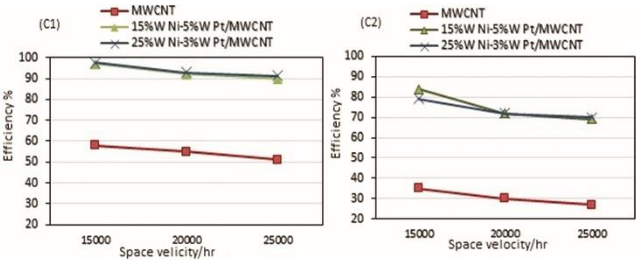


Figure 8. NO_2 removal efficiency profiles over prepared catalysts MWCNT, 15%W.Ni-5%W.Pt/MWCNT, 25%W.Ni-3%W.Pt/MWCNT at a space velocity of 25000, 20000, 15000/hr and concentration of 3000, ppm and (C1) temperature of 300 ° C (C2) temperature of 150 °C

3.7. Catalytic reduction

The use of water vapor as a nitrogen-reducing agent in various studies showed that water vapor has a substantial role in catalytic reduction; in the SCR process, it has the highest effect on the production of N_2, compared to the N_2O, in the NO_x removal process (Yang *et al.*, 2014; Qi *et al.*, 2003). On the other hand, in the oxidation process of nitrogen oxides, the water vapor has not played an active role (Xiong *et al.*, 2015). In this study, the water vapor has considered due to the advantages of water vapor in the removal of the nitrogen oxides and its conversion into a safe form. Some of the possible NO_2 reduction processes have shown below.

(A)

(a) $4H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(b) $4NO_2 + 4H^+ + 4e^- \rightarrow N_2 + H_2O$

a + b: $4NO_2 \rightarrow N_2 + 2O_2$

(B)

(c) $2C + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$

(d) $2NO_2 + 8H^+ + 8e^- \rightarrow N2 + 4H_2O$

c + d: $2C + 2NO_2 \rightarrow 2CO_2 + N_2$

(C)

(e) $4H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(f) $2NO_2 + 6H^+ + 6e^- \rightarrow N_2O + 3H_2O$

(g) $N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$

The reduction of NO_2 on the Ni-Pt/MWCNT catalysts depends on the absorption and re-absorption of H_2O and NO_2 on the catalyst and the ability of this catalyst in the oxidation of H_2O. The above reactions indicate that the water vapor, as a reducing agent, is oxidized on the surface of the catalyst and resulted in the production of hydrogen ions. Absorption of these hydrogen radicals on the active centers of the catalysts is resulted in reducing the nickel and platinum particles on the catalyst; this reduction in the electron density of metals on the catalyst leads to weakening of the oxygen-nitrogen bonds in the NO_2 and ultimately, formation of N_2, CO_2, H_2O, O_2, N_2O.

Studies have shown that the formation of N_2O on the catalyst is due to the formation of nitrogen radical on the catalyst that reacts with another phase of NO_2 or NO (Burch *et al.*, 2002). On the other hand, studies have shown that the production of CO and CO_2 on the catalyst at temperatures above 450 K and high pressure is led to the formation of CO and CO_2 by creating a gap in carbon nanotubes (Vermisoglou *et al.*, 2011). In this study, the formation of CO and CO_2 is limited due to the absence of gas pressure, and the duration of the calcination of the substance.

3.8. Effect of nickel and platinum weight percent on removal efficiency

The comparison of the catalytic removal of NO_2 by Ni-Pt/MWCNT with different weight percentage illustrated that the highest removal efficiency is obtained by 25%.W.Ni-3%.W.Pt/MWCNT catalyst at a similar temperature, concentration, and space velocity conditions. The results of this study showed that the weight percentage of nickel and platinum on MWCNT has remarkable importance so that increasing 10% w.t of nickel and decreasing 2% w.t of platinum are led to greater removal efficiency compared to the catalyst with 15% W.Ni and 5%W.Pt; this can be important in the synthesis of catalyst.

In the 25%W.Ni-3%W.Pt/MWCNT, the use of the higher weight percentage of nickel nanoparticles, as a non-noble metal, along with lower weight percentage of platinum showed higher NO_2 removal efficiency compared to the 15%W.Ni-5%W.Pt/MWCNT, which is important for catalyst synthesis and spent costs. Figure 7 depicts that increasing the concentration at high temperatures is not associated with significant changes in the efficiency of 25%.W.Ni-3%.W.Pt/MWCNT catalyst. But, in the 15%.W.Ni-5%.W.Pt/MWCNT catalyst, increasing the concentration has led to decreasing the efficiency, which it revealed the catalytic activity of nickel at the high temperatures (300–400 °C). The NO_2 conversion reactions showed that there is a greater difference between the removal efficiencies obtained by the catalyst with 3%W platinum and 25%W nickel and the catalyst with 15%W platinum and 5%W nickel at the space velocities of 15000 and 20000/ hr at high concentrations compared to the lower concentration, which it can be due to the weight percentage of active particles of catalyst at lower space velocities.

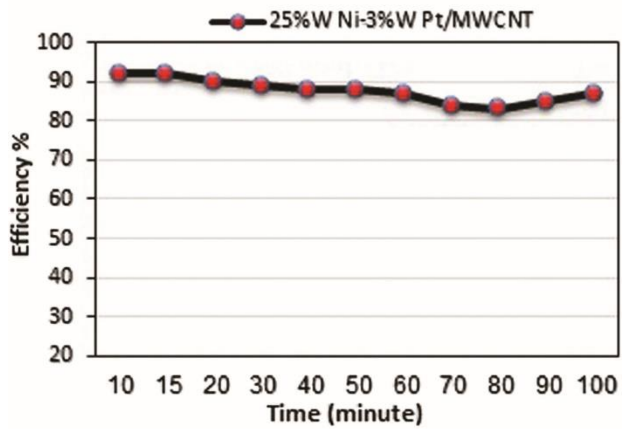


Figure 9. NO_2 removal efficiency profiles over prepared catalyst 25%W.Ni-3%W.Pt based on MWCNT. Concentration NO_2 3000 ppm and Space Velocity 25000/hr

According to the conducted experiments and regarding the high efficiency, temperature limitation and energy and cost benefits in catalysts, the best conditions for removal of NO_2 were the temperature conditions of 300 °C, space velocity of 25000/hr and concentration of 3000 ppm. The results of the removal efficiency of the second type of catalyst were measured during the catalytic reduction. The results of the experiments by the time are shown in Figure 9. With regard to the limitations, our results showed the 10% reduction in efficiency during the test time, which is consistent with the results of in Siwei Pan *et al.*; they studied the selective catalytic reduction of NO_x in the presence of water vapor using the MWCNT catalyst and observed that the reduction in efficiency of catalyst was approximately 10% over the initial period (Chen *et al.*, 1998).

4. Conclusion

The results of the experiments showed that the removal efficiency has significantly increased by supporting the nickel and platinum nanoparticles on the carbon nanotubes; so that, the Ni-Pt/MWCNT catalyst had high removal efficiency at NO_2 concentrations higher than 3000 ppm. Furthermore, the results showed that the use of water vapor as a reducing agent could have a significant effect on the removal efficiency. The presence of some impurities in carbon nanotubes and oxygen-containing functional groups in the catalyst bed can play a remarkable role on catalytic activity and removal efficiency. The results also showed that the catalysts with different weight percentages, at different temperatures, had a one percent change in efficiency; this indicates the low effect of space velocity on the removal efficiency and the greater effect of temperature on the removal efficiency obtained by both Ni-Pt/MWCNT catalysts. Concentration is another factor affecting the NO_2 removal efficiency so that the removal efficiency declines by an increase in the concentration, but there was no linear relationship. The weight percentage of metal particles on the catalyst is helpful in reducing the economic costs. The use of noble metals in the catalyst involves the imposition of high costs and the use of non-noble metals provides high efficiency at high temperatures; these deficiencies can be somehow eliminated by application of bimetallic catalysts.

Conflicts of interest

Authors have no conflicts of interest.

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